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14. ABSTRACT  The primary objective of this contract is to impart CWA neutralization capability into hydrogels with proven efficacy in the physical decontamination of radiological, TICs, TIMs and other contaminants, to achieve efficient decontamination of CWAs that have absorbed into sorptive substrates, via physical removal, neutralization or both. A further objective is to develop strategies to impart bactericidal and sporocidal capability into the systems developed with the ultimate objective being the development of a single CBRN system that will be effective against CWAs and BWAs as well as radiological contaminants, TICs and TIMs. The development of several formulations (both one-component and two-component systems) that demonstrate significant neutralization efficacy against VX, G-agents, and mustard gas simulants in solution and in substrate testing has been achieved. Screening evaluations of a variety of catalyst systems against CWA simulants performed during the initial quarters (Quarters 1 and 2) of this initiative demonstrated that the lanthanide catalyst systems had superior performance as compared to the other catalysts under evaluation. These lanthanide catalyst systems were further modified via adjustment of the type/concentration of lanthanide ion salts and/or the incorporation of a variety of components such as co-solvents, emulsifiers, and other additives to improve their neutralization efficacy on a variety of contaminant/substrate combinations. These modifications have resulted in the development of lanthanide catalyst systems that show enhanced neutralization rates against CWA simulants, approaching a 2-log reduction (99%+ decontamination efficacy) of initial challenge, when used as one-component systems (independent of the hydrogel component) or as two-component systems when combined with the DeconGel hydrogel template (either mixed before use or applied in sequence).					
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## **1. Introduction**

The purpose of this contract is to develop a decontamination system for medical operations for through or clearance level decontamination of medical facilities and assets that have been contaminated directly via enemy action, or via cross contamination from improperly decontaminated personnel. The decontamination system should be able to decontaminate nuclear and radiological contaminants, chemical warfare agents (CWAs), toxic industrial chemicals (TICs) and toxic industrial materials (TIMs) on porous, non-porous and sorptive substrates, under wet and dry conditions. This effort was undertaken to address decontamination concerns/requirements not currently addressed by decontamination research and development. A specific and unique objective is to impart neutralization capability into an already proven commercial hydrogel technology with demonstrated efficacy in the physical decontamination of radiological, TICs, TIMs and other contaminants. Additionally, to achieve efficient decontamination of CWAs that have absorbed into sorptive substrates, via physical removal, neutralization or both. A further objective is to develop strategies to impart bactericidal and sporicidal capability into the systems developed with the ultimate objective being the development of a CBRN system that will be effective against CWAs and BWAs as well as radiological contaminants, TICs and TIMs.

## **2. Executive Summary**

The research team made remarkable progress in integrating a commercial technology with state-of-the-art research and development of catalyst systems that demonstrate significant neutralization efficacy against VX, G-agents, and mustard gas simulants.

There is credible evidence, based upon research performed so far, that it is quite possible to develop a decontamination system effective against CWA, BWA, Radioisotopes, TICs, TIMs while still retaining fairly safe to use and handle characteristics.

Screening evaluations of a variety of catalyst systems against CWA simulants demonstrated that the lanthanide catalyst systems had superior performance compared to other catalysts under

evaluation. The team modified the type/concentration of lanthanide ion salts and incorporated a variety of components such as co-solvents, emulsifiers, and other additives to improve their neutralization efficacy on a variety of contaminant/substrate combinations. These modifications have resulted in the development of lanthanide catalyst systems that show enhanced neutralization rates against CWA simulants when used as one-component systems (independent of the commercial DeconGel component) or as two-component systems when combined with the DeconGel hydrogel template (either mixed before use or applied in sequence).

Solution test evaluations against the G-agent simulant (DPPC) as well as the mustard agent simulant (CEES) demonstrate that they are readily neutralized by lanthanide ion catalyst systems or components thereof. A notable achievement includes the development of an improved lanthanide catalyst system (Component A) that demonstrates fast neutralization rates and tolerance to water (>99% destruction of LG61 in the presence of 50% water by volume).

The commercial DeconGel hydrogel template has the ability to encapsulate and physically remove radioactive isotopes and Toxic Industrial Chemicals (TICs) from a variety of porous and non-porous substrates. A two-component decontamination system provides the medical end-user with several options: applying either component independent of the other when the threat is known, combining the two components in sequence or as a pre-mixed emulsion when the threat is unknown or when concurrent threats are present (e.g., radioactive isotopes and CWA threats from a ‘dirty bomb’).

Significant decontamination efficacy on Styrene Butadiene Rubber (SBR) substrates was achieved. Developed formulations demonstrate decontamination efficacy of >91% after 2 hours for a one-component system, and >96% after 24 hours for a two-component system mixed at the point of use, against LG61 on SBR. SBR is a notoriously difficult to decontaminate substrate due to its porous, sorptive and hydrophobic nature.

The majority of testing was performed on panels coated with Chemical Agent Resistant Coating (CARC). CARC, though more resistant to CWAs relative to other types of paint, is a highly porous and sorptive material that is difficult to decontaminate. An unexpected result observed

during evaluations on CARC coated coupons was the relatively large variation in the decontamination efficacy results of the lanthanide catalyst systems against LG61 on CARC coupons acquired/prepared from different sources. Efficacy results for one and two component decontamination systems have ranged from ~80% to 99%+ for evaluations performed on different batches of CARC coated coupons. To date, no satisfactory explanation has been determined for these decontamination efficacy inconsistencies on CARC coated coupons.

While two-component systems (mixed at the point of use, or applied sequentially) show decontamination efficacies of >99% against LG61 on stainless steel (SS), the lanthanide catalyst system (Component A) shows <99% efficacies on SS (2 hours of contact) when it is used independently of the hydrogel component. Recent tests performed on glass slides indicate that the reason for these lower efficacies on non-porous substrates may be originating from the surface tension of the CWA simulant (LG61 remains in the form of a droplet when applied on glass and steel). The result is a local concentration of CWA far greater than the 50:1 decontaminant to contaminant challenge target. Techniques to better dissolve the CWA as well as to apply a thicker layer of neutralization solution on the substrate are currently being developed and are expected to improve neutralization efficacies against CWAs on non-porous substrates.

CBIP is currently finalizing details for the first set of live agent testing. CWA simulants used in this study are less reactive than their live agent counterparts. Formulations that provide neutralization/decontamination results that achieve or approach the decontamination objective (2-log reduction of initial challenge) are anticipated to demonstrate equal or better results when tested against live agents.

Important achievements to date:

- Developed CWA neutralization (one-component) systems demonstrating 99%+ destruction of CWA simulants in solution tests.
- Developed CWA neutralization (one-component) systems achieving or approaching a 2-log reduction (99% decontamination) of initial challenge on a variety of substrates.

- Developed a catalyst system that demonstrates fast neutralization rates in the presence of water (99%+ destruction of VX simulant in the presence of 50% water by volume).
- Developed and demonstrated compatibility between the CWA neutralization catalyst system and the hydrogel (DeconGel) component.
- Developed two-component decontamination systems that can physically remove radioactive isotopes, TICs and other contaminants from substrates achieve or approach a 2-log reduction (99% decontamination) of initial CWA challenge on a variety of substrates.
- Demonstrated significant decontamination efficacy against the VX simulant on sorptive substrates such as SBR and CARC, approaching 99% decontamination.
- Conducted initial proof of concept studies demonstrate compatibility between BWA neutralizers (known sporicidal components) and the CWA neutralization systems developed to date.

### **3. Task 1: CWA Neutralization Catalyst Systems (100% Complete)**

Task 1 is complete.

The primary objective of Task 1 was to acquire and/or synthesize various catalytic systems that catalyze the neutralization/hydrolysis of CWAs and evaluate their efficacy against CWA simulants. Screening of the neutralization efficacy of these technologies in both solution and substrate tests led to the selection of the lanthanide catalyst systems for incorporation in the hydrogel template. A brief summary of the primary catalyst technologies of interest that have been evaluated for incorporation into the DeconGel hydrogel template can be found below under each subtask.

Initiation/completion of Task-1 was delayed due to changes in CBIP's staffing, and the significant maintenance and repair of analytical instrumentation used in this project. Although evaluation of efficacies of the proposed catalytic systems (individual catalysts and in



combination with the hydrogel template) against CWA simulants (Task 1) has been completed, initiation/completion of subsequent tasks (Tasks 2 and 3) was delayed.

### **3.1 Task 1(a) – Acquire and/or Synthesize Tailored Catalyst Systems that Efficiently Neutralize CWAs**

The catalytic compounds/systems that have been evaluated for incorporation into the hydrogel template can be divided into three categories. These include the lanthanide catalyzed alcoholysis (lanthanum/samarium technology from Queens University, Canada), dialkylamino pyridines (DAAPs, both monomeric and oligomeric/polymeric structures) and imidazoles (nucleophilic catalysts), and peroxy-generating compounds. All catalytic systems or components thereof have been acquired or prepared in-house, as needed, for the CWA neutralization evaluations.

#### **3.1.1 Lanthanide Catalyzed Alcoholysis**

The lanthanide catalyst decontamination technology involves a metal ion (lanthanum or samarium) catalyzed alcoholysis. The neutralization reaction is extremely fast when in non-aqueous solutions, and in contrast with other neutralization technologies that destroy CWAs by hydrolysis, this technology does not require the presence of water for activation. This is valuable in environments where little to no moisture is present (desert) and/or the substrate to be decontaminated is very hydrophobic. While this non-aqueous environment is favorable for increased surface contact between the neutralizing agent(s) and the hydrophobic CWAs, it presents challenges in wet environments because of possible hydrolysis reaction of the metal ion compound (destruction of the catalyst) which competes with the alcoholysis of the organophosphorus compound (destruction of the CWA) in the presence of high quantities of water. Evaluations on these lanthanide systems and modifications thereof have been performed in the presence and in the absence of water, and in one- and two-component systems. These lanthanide catalyst systems have demonstrated superior performance among all catalyst technologies evaluated during Task-1.

### 3.1.2 Dialkylamino Pyridines and Imidazoles

Many researchers have shown that dialkylamino pyridines (DAAPs) have impressive neutralization rates against electrophilic phosphate nerve agents and other cholinesterase inhibitors as well as mustards and related blister agents, chloroformates, phosgene, methyl isocyanates, acetyl chloride, acetic anhydride, and many other Toxic Industrial Chemicals (TICs) (1-3). Although water is required and consumed during the reaction, the rate does not depend on the concentration of water above a minimum stoichiometric requirement. Catalysts that have been acquired or synthesized and evaluated for their neutralization capability against CWA simulants include monomeric structures such as dimethylamino pyridine as well as oligomeric and polymeric structures, which are reported to have increased efficacy as compared to their monomeric starting materials. Imidazole-based compounds -similar in structure to DAAPs- are heterocyclic aromatic amines (with low toxicity/corrosiveness and high solubility in both aqueous and polar organic solvents) which have been shown to catalyze the hydrolysis of many CWAs. An inherent advantage of these imidazole-based compounds is their miscibility and diffusion in both hydrophobic and hydrophilic materials. Several imidazole-based compounds including imidazole, 1-methyl imidazole, 1-(3-aminopropyl)imidazole and 1-(p-toluenesulfonyl)imidazole have been evaluated for their neutralization capability against CWA simulants. Data show that DAAP and imidazole based catalytic systems perform well against G-agents simulants but showed far inferior performance against the VX simulant when compared to the lanthanide ion catalyst systems.

### 3.1.3 Peroxy Containing/Generating Compounds

Peroxy-containing or peroxy-generating compounds are under evaluation for their feasibility to be used in the future development of adding sporicidal and bactericidal properties to the compositions developed under this contract. Peroxy compounds are known to have sporicidal properties as well as the ability to neutralize most CWAs by oxidation (4, 5). A technical challenge that is inhibiting the utilization of these compounds is their tendency to decompose in a relatively short period of time when in

solution or in the presence of moisture and multivalent metal cations, which subsequently results in difficulties related to pre-deployment, storage and shipping. The peroxy containing/generating compounds that being evaluated under this contract are in dry powder form (for increased shelf-life stability) and are activated upon contact with water. Among others, peroxy-containing or peroxy-generating compounds that have been acquired and that will be evaluated for their decontamination efficacy against CWAs (and BWAs in the 2<sup>nd</sup> year) include potassium peroxymonosulfate, sodium perborate, and sodium percarbonate. Peroxy-containing or peroxy-generating compounds have shown far inferior performance against CWA simulants compared to the lanthanide catalyst systems. Evaluation of their sporicidal activity against BWA surrogates (*B. Subtilis* spores) will take place in the 2<sup>nd</sup> year of this contract.

### **3.2 Task 1(b) – Evaluate Hydrophilic and Hydrophobic Catalysts with Differing Solubilities/Solvent-Phase Partitions**

The primary objective of this initiative is to impart CWA neutralization capability in the hydrogel technology platform, and to utilize multiple catalysts or catalyst forms (hydrophilic and hydrophobic catalysts with differing solubilities) to achieve activity on and in hydrophilic (wet substrates) and hydrophobic (hydrophobic sorptive substrates) environments.

The catalyst technologies that have been evaluated during Task-1 neutralize CWAs via different chemical mechanisms that are efficient under different conditions, e.g., DAAP technology is efficient in polar aprotic media (organic solvents) and requires water (trace amount is adequate) to be activated, whereas the metal (lanthanum or samarium) catalyzed alcoholysis system is more efficient in non-aqueous environments and does not require the presence of water. At the beginning of the contract it was expected that these two technologies would be complementary to each other and would behave in a synergistic way, each circumventing deficiencies of the other. DAAP systems, however,

demonstrated lower than expected efficacies against the VX simulant (LG61) and have currently been disregarded from further evaluations.

Nonetheless, the development of a lanthanide catalyst neutralization technology (previously thought to provide adequate neutralization rates in low moisture environments) that shows fast neutralization rates under both anhydrous conditions and in the presence of water has been developed during the 1<sup>st</sup> year of this contract via the incorporation of multiple lanthanides. Details are given in later sections of this report.

### **3.3 Task 1(c) – Evaluate Hydrolysis (or Alcoholysis) Rates on CWA Simulants of Individual Catalysts**

Evaluations of hydrolysis (or alcoholysis rates) against CWA simulants of individual catalysts in both solution and substrate tests have been completed. Due to the toxicity of the actual CWAs, efficacy evaluations of the various catalytic systems and formulations have been performed on CWA simulants.

#### **3.3.1 Test on Porous, Non-Porous and Sorptive Substrates**

Select catalyst technologies (lanthanide catalyst systems) that demonstrated superior neutralization efficacy in solution tests (as compared to other catalyst technologies investigated) were further evaluated against CWA simulants on porous and non-porous substrates. More details are given in section 3.3.3.

#### **3.3.2 Test Neutralization of V, G and Mustard Agent Simulants**

Efficacy evaluations of the various catalytic systems and formulations have been performed on CWA simulants which mimic the reactivity and the physical and

chemical behavior of the actual CWAs. Some details on each of the CWA simulants utilized in this work are summarized below.

#### 3.3.2.1 VX Simulant

O,S-Diethyl Methylphosphonothioate (LG61) is being utilized as the VX agent simulant. LG61 is an ideal simulant for VX neutralization evaluations as related to military requirements. As a general rule of thumb, if something can hydrolyze/neutralize VX, then it will be effective against all V-agents and G-agents, since the latter are less persistent and easier to hydrolyze/neutralize as compared to VX. The majority of evaluations during the formulation development work has been performed against LG61 since VX and its simulants are the most difficult to neutralize/decontaminate.

#### 3.3.2.2 G-Agent Simulants

Diphenylphosphoryl Chloride (DPPC), which is considered to be a good simulant for G-agents, has been utilized during these evaluations. To increase confidence in the neutralization efficacy results of the catalytic systems developed for this project against G-agents, CBIP will also perform evaluations against DMMP. O,O-dimethylmethylphosphonate (DMMP) is a G-agent simulant whose physical properties very closely model those of widely-used G-agents although it is considered more difficult to neutralize. Discussions with JPEO-CBD have revealed that the most meaningful data for the military can be generated if G-agent simulants are mixed with thickening agents for persistency. CBIP has recently acquired a thickening agent suggested by JPEO-CBD; future evaluations will also be performed on thickened DMMP and DPPC simulants.

### 3.3.2.3 Mustard Gas Simulant

2-chloroethyl ethyl sulfide (CEES) is currently being used as a sulfur mustard simulant. CEES, a.k.a., “half mustard”, is an ideal simulant because its structure, reactivity and physical properties are similar to mustard agents.

## **3.3.3 Determine Neutralization Kinetics of Individual Catalysts**

### 3.3.3.1 Neutralization Efficacy of Individual Catalysts in Solution

The majority of initial screening evaluations of catalyst technologies have been conducted in solution (vial) testing. All screening trials were conducted at a decontaminant to contaminant volume ratio of 50 to 1 which is the military standard of decontaminant to contaminant ratio utilized for the evaluation of decontamination technologies against CWAs (4). Table 1 below summarizes decontamination efficacy data for select catalyst systems evaluated for their neutralization efficacy against CWA simulants. Decontamination efficacy results shown as greater than (>) are either results for which the analyte of interest was not detected, or the result was below the lowest concentration analyzed in the applicable calibration curve (i.e., below the limit of detection). Volume ratios utilized for the efficacy tests against DPPC in solution were 10 to 1 (decontaminant to contaminant ratio), which far exceeds the military standards (50 to 1 decontaminant to contaminant ratio).

**Table 1 – Neutralization Efficacies of Individual Catalyst Systems against CWA Simulants in Solution (vial) Tests**

Neutralization System	LG61		DPPC	
	Contact Time	Neutralization Efficacy (%)	Contact Time	Neutralization Efficacy (%)
System 4 (1)	2h	>89.4	<5m	95
System 8 (2)	10m	>99.9	<5m	94.2
System 12 (3)	10m	99.3	<5m	>89.88
DMAP - ETA (4)	2h	14.3	<5min	94.1
DMAP - DCM (4)	2h	none	<5min	94.2
Imidazole - DCM (4)	17h	10.6	~4h	26

<b>NMI - DCM (4)</b>	17h	none	~4h	9
<b>Imidazole - ACN (4)</b>	17h	13	~4h	92.1
<b>NMI - ACN (4)</b>	17h	none	~4h	93.7
<b>TSI - ACN (4)</b>	17h	none	~4h	94
<b>Oxone (5)</b>	17h	1.6	1h	14
<b>H2O2 (6)</b>	17h	none	1h	17.6
<b>DAAP System (7)</b>	24h	none	-	-

1) System 4 consists of La(OTf)<sub>3</sub> and an activator in Methanol

2) System 8 consists of La(OTf)<sub>3</sub> in Ethanolamine

3) System 12/M2 consists of Sm(OTf)<sub>3</sub> in Ethanolamine

4) Suffix of system name denotes solvent where ACN = Acetonitrile, DCM = Dichloromethane, ETA = Ethanolamine; prefixes denote organo-catalyst where the following apply: I = NMI = N-Methylimidazole, TSI = 1-(p-Toluenesulfonyl)imidazole, API = 1-(3-Aminopropyl)imidazole, and DMAP = Dimethylaminopyridine

5) Oxone was prepared as a 5% by weight aqueous solution

6) Hydrogen Peroxide 10% by weight in water

7) DAAP System: 0.07g/mL DAAP polymer in methanol, buffered to pH=9.2 using 0.1M aqueous tris buffer solution.

Among all the catalyst technologies evaluated during these screening evaluations, the lanthanide metal-based catalyst systems and components thereof (Systems 4, 8, 12) demonstrated superior performance with fast neutralization activity against VX, G-agents, and mustard gas simulants. As the above table shows, lanthanide catalyst systems were capable of achieving destruction of the LG61 >96% in less than 10 minutes, and destruction of DPPC >95% in less than 5 minutes in solution testing. Evaluations against the mustard gas simulant, 2-chloroethyl ethyl sulfide (CEES), demonstrated that CEES is readily soluble in ethanolamine (ethanol amine is the primary solvent in the lanthanide based catalyst technology) and that after 24 hours of exposure (50:1 volume ratio ethanol amine to CEES) to neat ethanolamine, >99% of the initial CEES present was neutralized.

The data above indicate that systems containing ethanolamine as the solvent (Systems 8 & 12) show faster rates compared to systems (System 4) that contain methanol as the solvent. ETA alone neutralizes DPPC with 80% efficacy in less than 5min, and CEES with 99% efficacy in 24 hours. Ethanolamine seems to be facilitating the neutralization reaction of the simulants either by partially neutralizing the CWA simulants, by facilitating neutralization of the CWA simulants due to the more nucleophilic character of ETA compared to methanol and/or water, or simply

by providing superior solubility for the CWA simulants used. Notably, the US Army has approved the use of ethanolamine based formulations due to its high flash point ( $\sim 85^{\circ}\text{C}$ ).

These data also show that monomeric dialkylaminopyridine (DAAP) and imidazole-based candidate catalytic systems perform well against DPPC (DEs  $>94\%$  in less than 5 minutes), but show far inferior performance against LG61 (DEs  $<20\%$  after 2 hours) when compared to the lanthanide ion catalyst systems. These systems have been removed from further consideration for incorporation into the hydrogel template. Lastly, evaluations of a variety of peroxy-containing or peroxy-generating technologies showed poor performance against chemical warfare agent (CWA) simulants in initial vial tests. However, these neutralization systems were evaluated in the absence of components such as cosolvents, emulsifiers, or activators. Future work (2<sup>nd</sup> year) will include the incorporation of components that aid in the emulsification/interaction of peroxy-generating or peroxy-containing compounds with CWAs (and their simulants), and evaluation of their neutralization activity against CWA simulants and BWA surrogates.

During the screening evaluations of the individual catalyst systems, development efforts focused on VX and G-agents simulants. Out of all CWAs, VX and its simulants are considered to be the most persistent and most difficult to hydrolyze/neutralize (7, 8). Catalyst systems are expected to have greater efficacy against mustard gas (and simulants) since the latter are easier to hydrolyze/neutralize as compared to V-Agents (specifically VX).

#### 3.3.3.2 Neutralization Efficacy of Individual Catalysts on Substrates

The lanthanide catalyst systems that demonstrated optimum performance against CWA simulants in solution (vial) tests were further evaluated (in 2<sup>nd</sup> Quarter) against the VX simulant (LG61) on substrates. Table 2 below summarizes decontamination



efficacy results of individual lanthanum triflate catalyst systems (System 8) against LG61 on CARC, stainless steel, and rubber substrates.

**Table 2 – Neutralization Efficacies of Individual Catalyst Systems against LG61 (VX simulant) on Multiple Substrates**

Neutralization System	Substrate	Contact Time	Initial Challenge (g/m <sup>2</sup> )	Residual Challenge (g/m <sup>2</sup> )	Neutralization Efficacy (%)
<b>Modified System 8 (100mM)</b>	Stainless steel	1h	5.949	0.748	87.4
<b>System 8</b>	CARC	10m	14.374	0.82	94.3
<b>System 8</b>	CARC	60m	14.374	0.31	97.8
<b>Modified System 8 (100mM)</b>	Rubber (SBR)	1h	5.949	1.454	75.6

The above catalyst systems have been further improved and have demonstrated fast neutralization rates against CWA simulants when used independently (only the non-aqueous component) or in combination with the hydrogel component (mixed before use or applied sequentially) achieving or approaching a 2-log reduction (99% reduction of initial challenge) in substrate tests (refer to Task-2 for more details).

#### **4. Task 2: Develop Two-Part Systems and Emulsion Systems with Preferred Catalysts (90% Complete)**

Development and efficacy evaluations of two-component and emulsion decontamination systems have provided very promising results. One-component, two-component, and mixed (emulsion) systems have successfully been developed and demonstrated close to a 2-log reduction of initial challenge (99% decontamination efficacy) on a variety of substrates including CARC, rubber (SBR), and stainless steel.

As described previously, among the catalytic systems evaluated during the screening evaluation step (Task-1), the lanthanide catalyst systems demonstrated superior neutralization ability. These systems showed superior performance when ethanolamine was the main solvent. Additionally, various co-solvents augmented the performance of these systems on various substrates against

CWAs. Modified non-aqueous lanthanide decontamination systems have been evaluated independently (i.e., application of non-aqueous catalyst system Component A only) and in combination with the DeconGel template both in sequential application method systems (i.e., application of Component A followed by the application of the hydrogel system Component B), and in mixed systems (i.e., lanthanide systems mixed with the hydrogel component at the point of use).

A notable achievement during Task-2 includes the development of a lanthanide catalyst system (Component A) that demonstrates fast neutralization rates and tolerance to water (>99% destruction of LG61 in the presence of 50% of water by volume). This system is a mixture of two lanthanide salts (lanthanum and samarium triflates) and combines the fast neutralization rates of the lanthanum system (System 8) and the tolerance to water of the samarium system (System 12). This achievement expands the versatility of these catalyst systems as it further broadens the conditions under which the catalyst is effective (e.g., damp/wet). It also offers the option to utilize them in combination with the water-based hydrogel component (Component B) both in premixed systems (the two components are mixed at the spray tip) or systems that are applied sequentially (application of Component A followed by the application of Component B).

The DeconGel hydrogel template has the ability to encapsulate and physically remove radioactive isotopes and Toxic Industrial Chemicals (TICs) from a variety of porous and non-porous substrates. A two-component decontamination system that can decontaminate CWAs (Component A) and radioactive isotopes/TICs (Component B) provides the end user with several options: applying either component independent of the other when the threat is known; combining the two components in sequence; or, as a pre-mixed emulsion when the threat is unknown or there are concurrent threats present (e.g., radioactive isotopes and CWA threats from a ‘dirty bomb’).

#### **4.1 Task 2(a) – Utilize Solvents, Surfactants, and Synthetic/Formulation Techniques to Achieve Neutralization Activity in Hydrophilic and Hydrophobic Environments and on/in Sorptive Substrates**

Multiple co-solvents, surfactants, and emulsifiers are under evaluation for their efficacy on and in hydrophilic (e.g., wet substrates) and hydrophobic (e.g., hydrophobic sorptive substrates) environments. Development efforts focused on co-solvents that would make the lanthanide catalyst systems and the hydrogel template compatible, while concurrently assisting the neutralizing agents to penetrate porous and sorptive substrates (e.g. CARC and rubber) and access the absorbed CWAs.

Rubber is a sorptive material with a high affinity for hydrophobic compounds (the majority of CWAs) (8). As rubber substrates present a difficult challenge for chemical decontamination, the evaluations have focused mostly on solvent systems that have the ability to penetrate rubber. Among others, solvents that have been or will be evaluated for their ability to penetrate rubber, dissolve the lanthanide catalyst systems, and remain miscible with ethanolamine (the main solvent of the lanthanide neutralization system) include tetrahydrofuran (THF), ethyl lactate, dimethylsulfoxide (DMSO), acetonitrile (ACN), dipropylene glycol monomethyl ether, ethylene glycol monobutyl ether, N-methyl pyrrolidone (NMP), limonene, trichloroethylene (Perc), dimethoxy methane (DMOM), n-propyl bromide, and propylene carbonate as well as some petroleum distillates that are used for degreasing applications.

As will be described in later sections of this report, a modified lanthanide catalyst system that demonstrates fast neutralization rates and retains its decontamination efficacy in the presence of high amounts of water has been developed (vial tests show 99%+ decontamination efficacy against LG61 in the presence of 50% by volume of water). The co-solvents mentioned earlier will be (or have been) evaluated (independently and in combination) for incorporation into this catalyst system to further enhance its decontamination efficacy on rubber and CARC. Some of these solvents have shown very promising results and are currently under extensive evaluation for their ability to enhance

decontamination efficacy when incorporated into the lanthanide catalyst decontamination system. Additional details on the performance of these solvent systems, including their ability to absorb into rubber, remain miscible with ethanolamine, and provide shelf-stable decontamination systems are provided in Appendix 2. A catalyst system (non-aqueous, Component A) that comprises 80% ethanolamine, 10% THF, and 10% DMOM shows promising results. The addition of lipophilic co-solvents seems to be assisting in the solvation of the greasy CWA simulants deposited on the substrate. Physical properties such as the flash point and flammability profile of this system are currently under evaluation (a sample has been sent to an independent lab for flash point testing).

Quaternary ammonium salts (quat salts) seemed to be ideal candidates for incorporation into the lanthanide catalyst technology since they combine surfactant/emulsifying properties with biocidal activity. However, both vial and substrate testing indicated that these quat salts are not compatible with the lanthanide decontamination system. Decontamination efficacy results against LG61 in vials and on rubber show reduced neutralization rates of the lanthanide catalysts. Quat salts have been disregarded from further consideration.

#### **4.2 Task 2(b) – Determine and Develop Compatibility and Stability**

Evaluations of the compatibility and stability of one- and two-component decontamination systems have been performed. Solvent systems, such as dimethoxy methane, THF, and ethanolamine that demonstrate enhanced decontamination efficacy of the lanthanide catalyst systems provide stable homogeneous non-aqueous catalyst systems (Component A). While pre-mixed systems of Component A (non-aqueous lanthanide catalyst system) with Component B (hydrogel component) do not seem to provide a system that can retain its neutralization efficacy against CWAs for prolonged periods of time (~1 year), systems that are mixed right before use (e.g., at the spray tip) or are applied sequentially (Component A followed by Component B) have shown good compatibility.

### **4.3 Task 2(c) – Evaluate Hydrolysis (or Alcoholysis) Rates of CWA Simulants of Part A, Part B and Emulsion Systems**

Evaluations of the neutralization efficacy of Component A (catalyst system, non-aqueous phase), Component B (hydrogel template, aqueous phase), and two-component systems [Component A (non-aqueous phase) and Component B (hydrogel aqueous phase)] have been performed. Two-component systems are expected to enhance the versatility of the final product such that it can be more effectively applied in a wide variety of environments and substrates including wet or hydrophilic surfaces and hydrophobic/sorptive substrates such as rubber. More details are given in the following sections (Sections 4.3.1 – 4.3.3).

#### **4.3.1 Test on Porous, Non-Porous and Sorptive Substrates**

One-component and two-component decontamination systems have been evaluated on a variety of substrates including non-porous substrates such as stainless steel and glass, and porous and sorptive substrates such as CARC and rubber (Styrene Butadiene Rubber, SBR). As will be described in more detail in later sections of this report, a lanthanide catalyst system that comprises a mixture of samarium and lanthanum triflate salts has been developed. This has demonstrated superior performance with regards to its decontamination efficacy rates in the presence of water as compared to its counterparts that contain either just lanthanum (System 8) or just samarium (System 12) triflate salts. This improved system along with various other catalyst system candidates have been evaluated as one-component decontamination systems as well as in combination with the hydrogel component (two-component systems either mixed right before use or applied sequentially) on a variety of substrates.

#### 4.3.1.1 Decontamination Efficacy against CWAs on Non-Porous Substrates

While two-component systems (the lanthanide catalyst system and the hydrogel component mixed at the point of use, or applied sequentially) show decontamination efficacies of >99% against LG61 on stainless steel (SS), the lanthanide catalyst system (Component A) demonstrated <99% efficacies on SS (2 hours of contact) when used independent of the hydrogel component. For these unexpectedly low decontamination efficacies on stainless steel, it was postulated that the steel was affecting the catalytic efficacy of the lanthanide ions by partially reducing the lanthanide(III) ion to lanthanide(II) or other catalytically inactive species. To compensate for this issue on stainless steel substrates (as well as on other metal substrates that may present similar problems), modified lanthanide systems with an increased concentration of the lanthanide catalyst salts were utilized such that even if a sacrificial amount of the lanthanide ion were to be reduced upon contact with steel, the remaining amount of the lanthanide(III) active species would be adequate to retain the catalytic activity of the decontamination system. It is important to note that the application of the lanthanide ion catalyst system does not visually damage the steel substrate; no corrosion or destruction of the steel surface is observed.

Decontamination efficacy results of these improved lanthanide catalytic systems against LG61 on stainless steel can be seen in Table 3. System 10 (an improved lanthanide system with fast neutralization rates in the presence of water), which is a mixture of lanthanum triflate (50mM) and samarium triflate (50mM), shows decontamination efficacy against LG61 on stainless steel of ~73% and ~79% after 1 and 2 hours of contact respectively. System 10.2, which is a modification of System 10, shows improved decontamination efficacy against LG61 on stainless steel approaching ~94% after a 2 hour contact time.

Recent tests performed on glass slides indicate that the reason (or additional reason) for the lower efficacies of the lanthanide catalyst solution systems on non-porous substrates may be originating from the surface tension of the CWA simulant (LG61 remains in the

form of a droplet when applied on glass and steel). The result is a local concentration of CWA far greater than the 50:1 decontaminant to contaminant challenge target. Techniques to better dissolve the CWA as well as to apply a thicker layer of neutralization solution on the substrate are currently being developed and are expected to improve the neutralization rates against CWAs on non-porous substrates. Polymers and thixotropic agents will be evaluated for incorporation in the lanthanide catalyst systems to improve resistance of the (low-viscosity) lanthanide catalyst systems to spread and sag on horizontal and vertical substrates respectively, thus providing higher loads of catalyst per unit surface area.

**Table 3 – Decontamination Efficacies of Improved Lanthanide Catalyst Systems on Stainless Steel**

Decontamination System	Substrate	Contact Time	Initial Challenge (g/m <sup>2</sup> )	Residual Challenge (g/m <sup>2</sup> )	Decontamination Efficacy (%)
<b>System 10</b>	SS	1h	7.920	2.07	73.87 ± 11.03
<b>System 10</b>	SS	2h	7.920	1.61	79.65 ± 3.08
<b>System 10.2</b>	SS	1h	7.920	0.92	88.38 ± 2.53
<b>System 10.2</b>	SS	2h	7.920	0.49	93.85 ± 3.02

Decontamination efficacies of one-component systems (non-aqueous catalyst system only) after extended contact times (e.g., 12 or 24 hours) are also currently being evaluated to determine if longer decontamination times are required for the complete neutralization of CWAs on non-porous substrates (when the hydrogel component is not utilized). Initial screening of a modified lanthanide catalyst system on SS demonstrates decontamination efficacies >99.9% after 24 hours of contact time.

Table 4 below summarizes decontamination efficacy results for two component systems against LG61 on stainless steel. Component A (non-aqueous phase) consisted of System 10 (mixture of La/Sm triflate salts, both at 50mM) or System 10.2 (mixture

of 200mM La triflate with 100mM of samarium triflate); Component B consisted of DeconGel 1128, a sprayable hydrogel formulation recently developed at CBIP optimized for increased efficacy against radioactive isotopes, hydrophobic contaminants, and TICs. These two-component systems were either mixed immediately before use (similar to mixing at the tip of a spray gun) or applied sequentially (Component A applied first followed after 2 hours by Component B) on top of the contaminated (with LG61) coupons, and allowed to dry for 24 hours before removal of the gel and analysis of the residual contaminant.

**Table 4 - Decontamination Efficacies of Two-Component Decontamination Systems Against LG61 on Stainless Steel**

Decontamination System	Substrate	Contact Time	Initial Challenge (g/m <sup>2</sup> )	Residual Challenge (g/m <sup>2</sup> )	Decontamination Efficacy (%)
<b>Two-part System Mixed Before Use. System 10 with DeconGel 1128</b>	SS	24h	7.920	0.01	99.88 ± 0.06
<b>Sequential Application of System 10 followed by DeconGel 1128 after 2hrs</b>	SS	24h	7.920	0.02	99.68 ± 0.08
<b>Two-part System Mixed Before Use. System 10.2 with DeconGel 1128</b>	SS	24h	7.920	0.01	99.94 ± 0.03
<b>Sequential Application of System 10 followed by DeconGel 1128 after 2hrs</b>	SS	24h	7.920	0.01	99.90 ± 0.02

The table above demonstrates that two-component decontamination systems are capable of providing >99% decontamination against LG61 on stainless steel coupons. These decontamination efficacy values are based on the analysis of the amount of the CWA simulant that remains on the substrate after peeling off the dried gel. Current efforts are focusing on analyzing CWA simulant encapsulated in the peelable gel that may remain un-neutralized. However, testing of lanthanide catalyst solutions against LG61 in the



presence of water (similar to the hydrogel component) indicate that the catalyst system is capable of achieving >99% decontamination even after 24 hours of water exposure at a 1:1 volume ratio (50% water by volume). As has been described earlier, two-component systems are expected to enhance the versatility of the final product such that it can be more effectively applied to a wide variety of environments including wet or hydrophilic surfaces and hydrophobic sorptive substrates such as rubber.

#### 4.3.1.2 Decontamination Efficacy against CWAs on Porous Substrates

The efficacy of the decontamination systems (both one and two component systems) developed under this contract have been evaluated on non-porous and sorptive substrates such as CARC and SBR. Chemical Agent Resistant Coating (CARC), though more resistant to CWAs relative to other types of paint, is a highly porous and sorptive material that is difficult to decontaminate. Decontamination of CWAs on (in) sorptive substrates is a significant challenge due to the difficulty of bringing the neutralization agent in contact with the absorbed CWA. The majority of substrate testing evaluations have been performed on CARC coated coupons.

An unexpected result observed during evaluations on CARC coated coupons was the large variation in the decontamination efficacy results of the lanthanide catalyst systems against LG61 on CARC coupons acquired/prepared from different sources. The Second and Third Quarter results indicated that the decontamination of CARC (coupons prepared by JPEO-CBD) for one-component systems (only the non-aqueous Component A applied) was in the 97%-99%+ range. During the 4<sup>th</sup> Quarter work however, decontamination efficacy against LG61 on CARC (coupons prepared in-house) decreased to about ~70-80% for one-component lanthanide catalyst systems. Several factors that may have caused the decrease in efficacy have been investigated. To date, no satisfactory explanation has been determined for these decontamination efficacy inconsistencies on CARC coated coupons. Current efforts continue to focus on determining the reason for the reduced decontamination efficacy results on CARC, and separately, on evaluation of additional co-solvents and additives that are expected to

enhance the decontamination efficacy on CARC and other sorptive substrates. Additional decontamination efficacy evaluations on alternative CARC coupons kindly provided by the Edgewood Chemical and Biological Center (ECBC) are currently underway.

The table below summarizes results for the decontamination efficacy evaluations of one- and two-component decontamination systems against LG61 on various batches of CARC coated coupons. As described earlier, efficacy evaluations performed on CARC coupons provided by JPEO demonstrated 99%+ destruction of LG61 for one-component systems (only the non-aqueous Component A applied) after 1 hour of contact. Decontamination efficacy results from evaluations performed in the 4<sup>th</sup> Quarter on CARC coupons from a different batch (prepared both by JPEO and in-house) show neutralization efficacies for one-component systems in the range ~80% against LG61 after 2 hours of contact time. Moreover, inconsistent results have been shown on CARC coupons from different batches for mixed and sequentially applied two-component systems. Table 5 shows that decontamination efficacy values range between 95% and 99%+ for two-component systems (mixed before use or applied sequentially) against LG61 on CARC coated coupons from different batches. Current efforts are focusing on the evaluation of additional co-solvents and additives that are expected to enhance the decontamination efficacy on CARC (and other sorptive substrates), as well as determination of the reason for the reduced decontamination efficacies on CARC as compared to results from earlier quarters.

**Table 5 - Decontamination Efficacies of One-Component and Two-Component Decontamination Systems Against LG61 on CARC coupons\***

Decontamination System	Substrate	Contact Time	Initial Challenge (g/m <sup>2</sup> )	Residual Challenge (g/m <sup>2</sup> )	Decontamination Efficacy (%)
<b>System 8 (100mM)</b>	CARC	10 min.	14.374	0.086	99.40 ± 0.77
<b>System 10.2</b>	CARC	2h	7.973	1.518	80.96 ± 3.24
<b>Modified System 8 (100mM, 20/80 THF/Ethanolamine)</b>	CARC	1h	14.176	0.055	99.61 ± 0.852
<b>Two-part System Mixed Before Use. System 10.2 with DeconGel 1128</b>	CARC	24h	7.973	0.352	95.59 ± 0.16
<b>Sequential Application of Modified System 8 (100mM, 20/80 THF/Ethanolamine) followed by DG1128 after 1hr</b>	CARC	24h	14.167	0.02	99.86 ± 0.086
<b>Sequential Application of System 10.2 followed by DeconGel 1128 after 2hrs</b>	CARC	24h	7.973	0.355	95.54 ± 1.47

\* CARC coupons from different batches have been utilized in these studies presenting inconsistencies between test runs performed in different quarters.

A very important advancement achieved during this contract's first year has been the exceptional decontamination efficacy against LG61 on rubber substrates. Styrene Butadiene Rubber (SBR) is a notoriously difficult to decontaminate substrate due to its porous, sorptive, and hydrophobic nature. Formulations currently under development demonstrate remarkable decontamination efficacy against LG61 on SBR. One-component systems (System 10.2) show decontamination efficacies >91% after 2 hours of contact against LG61 on rubber, whereas a two-component system (System 10.2 mixed with DeconGel 1128) shows >96% against LG61 on rubber. Select decontamination efficacy results for one- and two-component decontamination systems against LG61 on rubber can be seen in Table 6. The work aimed at identifying co-solvents, surfactants, and other additives that has been described earlier is an integral

part of the formula optimization and is expected to further enhance the decontamination efficacy on rubber, e.g., approaching a 2-log reduction of the initial challenge (>99% decontamination).

**Table 6 - Decontamination Efficacies of One-Component and Two-Component Decontamination Systems against LG61 on Rubber**

Decontamination System	Substrate	Contact Time	Initial Challenge (g/m <sup>2</sup> )	Residual Challenge (g/m <sup>2</sup> )	Decontamination Efficacy (%)
<b>System 10.2</b>	SBR	2h	7.973	0.657	91.40 ± 2.46
<b>Two-part System Mixed Before Use. System 10.2 with DeconGel 1128</b>	SBR	24h	7.973	0.283	96.43 ± 9.01

Decontamination results to date across the board demonstrate improvement of decontamination efficacy when Component A (non-aqueous catalyst component) is used in tandem with Component B (DeconGel hydrogel component). DeconGel is known to physically remove and encapsulate contaminants into its semi-crystalline polymer lattice.

#### **4.3.2 Test Neutralization of V, G and Mustard Agent Simulants**

As described earlier, the majority of evaluations of the neutralization efficacy of the decontamination systems developed thus far have been performed against LG61, which is a VX simulant. Decontamination efficacy results against the G-agent simulant diphenylphosphoryl chloride (DPPC) as well as the mustard agent simulant 2-chloroethyl ethylsulfide (CEES) indicate that they are readily neutralized by the lanthanide ion catalyst systems or components thereof. LG61 continues to be the main CWA simulant of interest since VX and its simulants are the most difficult to neutralize/decontaminate (7, 8). Full sets of evaluations against G-agents and

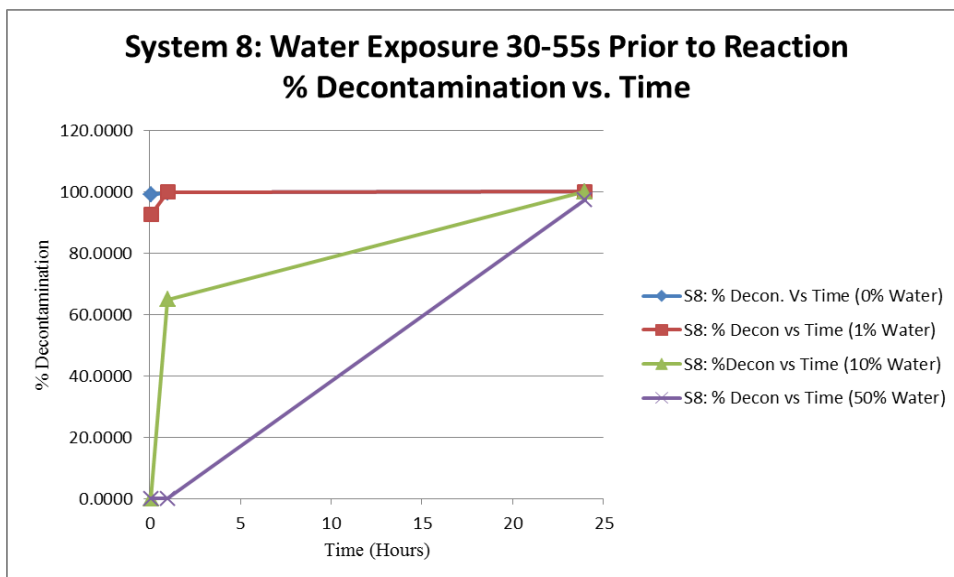
mustard gas simulants both in solution and on dry and pre-wetted substrates are currently underway.

#### **4.3.3 Determine Neutralization Kinetics via LC-MS & GC-MS Analysis**

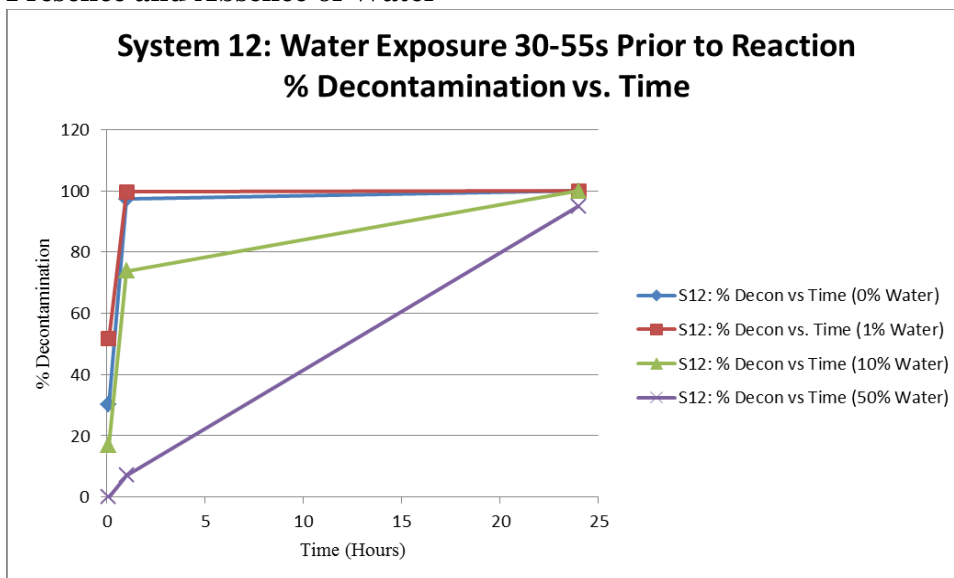
The neutralization kinetic rates of the lanthanide decontamination systems have been evaluated in solution (vial) tests against LG61. Lanthanide systems evaluated include: System 8, which comprises 50mM lanthanum triflate in ethanolamine; System 12 which comprises 50mM samarium triflate in ethanolamine; and System 10, which comprises a mixture of samarium and lanthanum triflate salts (50mM each) in ethanolamine. Neutralization kinetic rate evaluations were performed under anhydrous conditions as well as in the presence of water ranging from 1% to 50% by volume.

Triflate salts of lanthanide ions are known to be generally stable in water; however, water inhibits the catalytic activity of the lanthanide catalyzed neutralization of CWAs (phosphonate transesterifications) (9, 10). Rates determined in the presence of water relate to both the efficacy of the system in wet or high moisture conditions, and to the compatibility of the lanthanide catalyst system with the water-based DeconGel hydrogel template. Figures 1-4 below illustrate the relative reaction rates for Systems 8 and 12 (one-component catalyst systems).

**Figure 1 - Neutralization Kinetics of System 8 against LG61 in the Presence and Absence of Water**



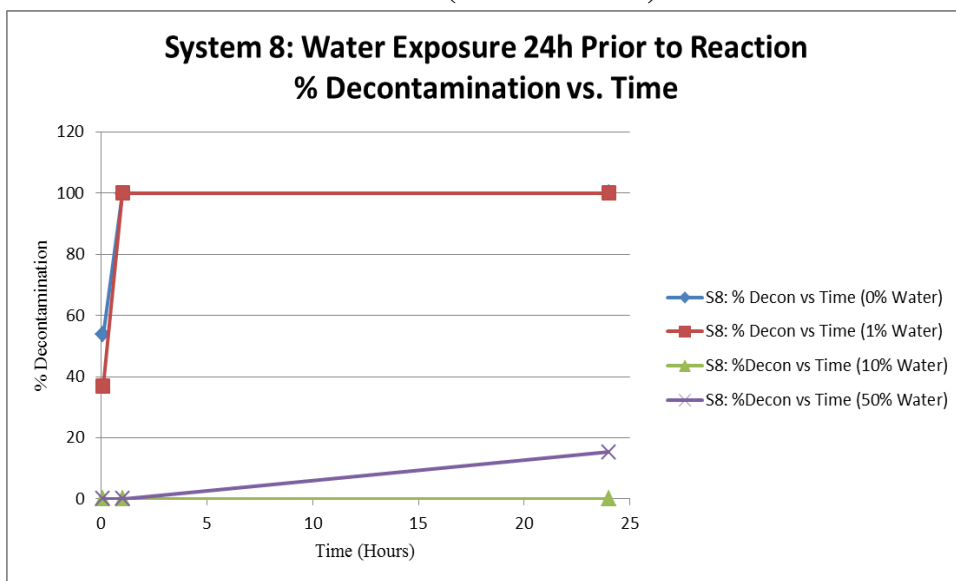
**Figure 2 - Neutralization Kinetics of System 12 against LG61 in the Presence and Absence of Water**



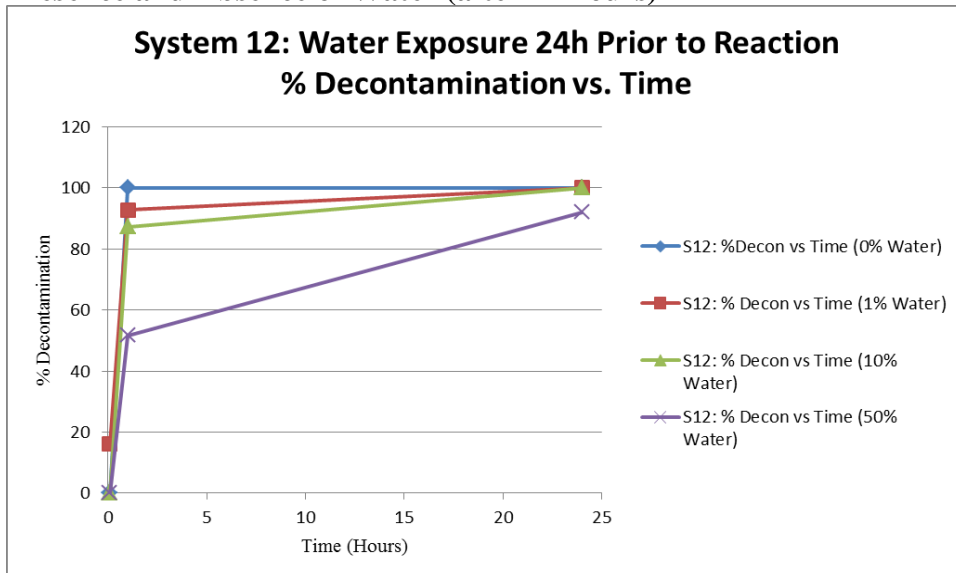
The above figures show that the initial rate for System 8 is faster than that of System 12 in the absence of water. However, when the water content exceeds 10% by volume, System 12 is more tolerant of the aqueous environment. In other words, the lanthanum triflate catalyst system (System 8) demonstrates faster neutralization rates in anhydrous (or low moisture) conditions, whereas the samarium triflate catalyst

system (System 12) demonstrates faster rates against LG61 in the presence of water. The neutralization rates of these systems were evaluated when the catalyst systems and water were mixed immediately before the test evaluations (Figures 1 and 2 above). Similar evaluations were performed on lanthanide systems that had been exposed to water for 24 hours before the test runs (Figures 3 and 4 below).

**Figure 3 - Neutralization Kinetics of System 8 against LG61 in the Presence and Absence of Water (after 24 hours)**



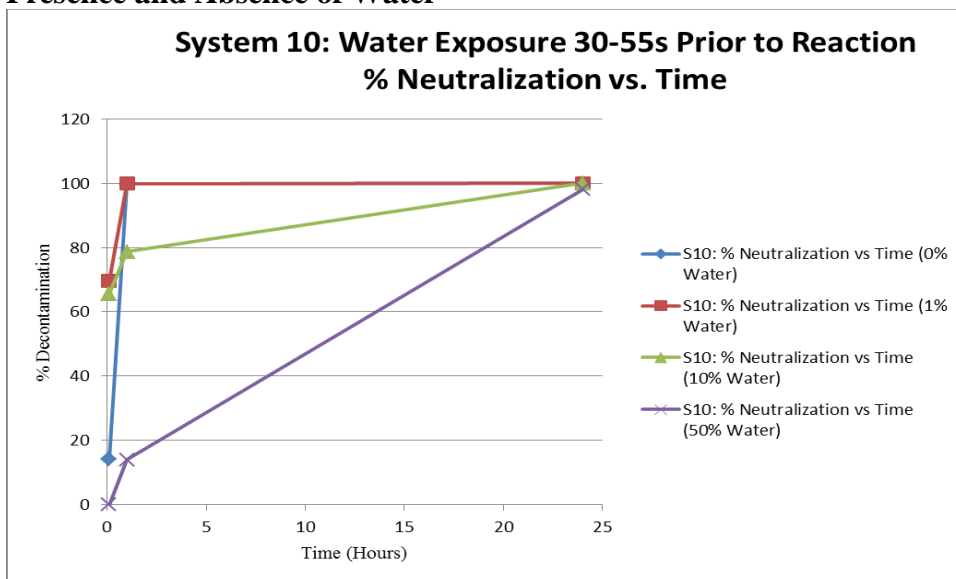
**Figure 4 - Neutralization Kinetics of System 12 against LG61 in the Presence and Absence of Water (after 24 hours)**



The figures above demonstrate that System 12 (samarium triflate) is more tolerant of water in excess of 1% by volume whereas System 8 (lanthanum triflate) seems to almost be deactivated when in contact with high loads of water after 24 hours.

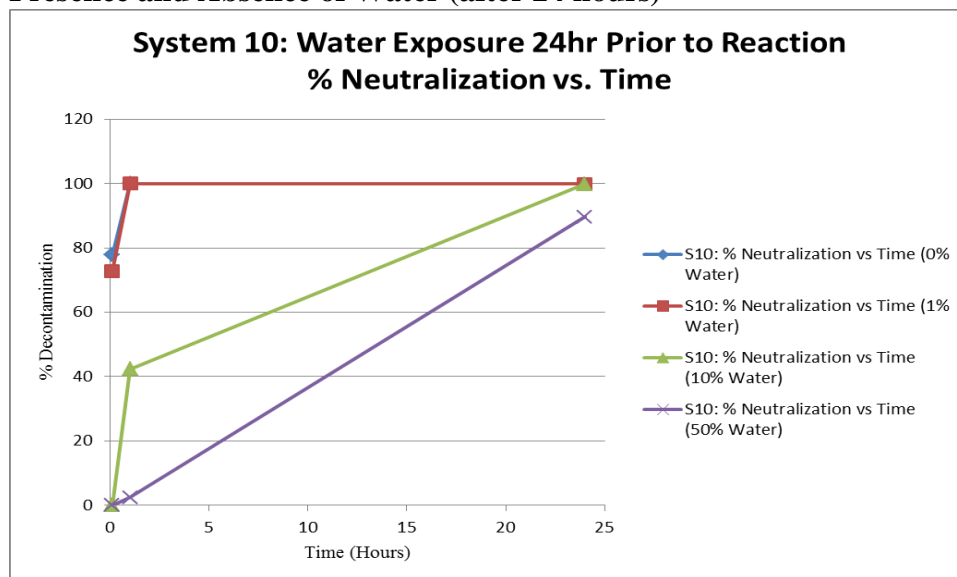
To take advantage of both the high initial catalytic rate of the lanthanum system (System 8) and the water tolerance of the samarium system (System 12), a modified system (System 10) was developed and evaluated for its neutralization efficacy rates in the presence and absence of water. This lanthanide system comprises a mixture of samarium and lanthanum triflate salts (50mM each). The figures below show the reaction rates for System 10 in the presence and absence of water. These evaluations were performed on systems that were brought into contact with water immediately before the neutralization rate evaluations (Figure 5) as well as on systems that were mixed with water 24 hours prior to the neutralization rate evaluations (Figure 6).

**Figure 5 - Neutralization Kinetics of System 10 against LG61 in the Presence and Absence of Water**





**Figure 6 - Neutralization Kinetics of System 10 against LG61 in the Presence and Absence of Water (after 24 hours)**



Above figures demonstrate that System 10 remains active even in the presence of high loads of water (up to 50% by volume) for 24 hours or more. This is a notable achievement since it expands the versatility of these catalysts systems by broadening their applicability to wet conditions as well as offering the option to utilize them in combination with the water-based hydrogel component in premixed systems (the two components are mixed at the spray tip), or in systems that are applied sequentially (application of Component A followed by the application of Component B). System 10 and a modified System 10 (System 10.2, containing higher concentrations of lanthanide salts) have been further evaluated in one- and two-component systems (mixed with the hydrogel component) on a variety of substrates; additional details have been given in earlier sections of this report (refer to Tables 3-6).

## 5. Task 3: Develop Two Systems for Chemical Live Agent Testing (20% Complete)

Two decontamination systems that have shown optimum good performance have been developed. These two systems that will be sent for live agent testing include System 10.2 (one-component system) and a two component system that will be comprised of System 10.2

(Component A) and DeconGel 1128 (Component B). It must be noted that from a chemistry and kinetics stand-point, LG61 is considered to be more difficult to neutralize than its live agent counterpart, VX (7, 8). Faster neutralization rates of the above two systems developed under this initiative are expected against VX compared to LG61 in-house trials.

### **5.1 Task 3(a) – Test Neutralization of Simulants on Both Dry and Pre-Wetted Substrates**

Evaluations of the two systems developed for the first phase of live agent testing on dry substrates including stainless steel, SBR, and CARC have been completed. Optimization efforts have been directed towards maximizing decontamination efficacy against greasy contaminants on dry substrate surfaces. Evaluations of these decontamination systems on pre-wetted substrates will also commence. Based on results demonstrating the water tolerance of System 10, it is expected that high level decontamination of pre-wetted substrates will readily be achieved.

### **5.2 Task 3(b) – Optimize Neutralization Activity and Stability**

Formulation efforts during this contract's first year have focused on optimizing neutralization efficacy by the enhancement of decontamination rates. This process has resulted in the development of System 10 to overcome water sensitivity issues, and System 10.2 containing increased concentrations of catalyst salts which subsequently demonstrated increased decontamination efficacies of a variety of substrates (as described in previous sections). Both of these systems are expected to be shelf stable. Long term stability studies on these and similar systems have started.

### **5.3 Task 3(c) – Submit to an Independent Laboratory for Live Agent Testing on Substrate/Agent Combinations Recommended by JPEO-CBD**

The two decontamination systems to be sent for the first phase of live agent testing have been identified. CBIP and CUBRC (the lab performing the live agent testing) are currently finalizing details for experimental matrix.

## **6. Task 4: Further Optimize Formulations of Chemical Live Agent Testing (0% Complete)**

First round live agent testing has not yet started.

## **7. Task 5: Neutralization Systems Against BWA Surrogates (10% Complete)**

Active catalytic destruction of BWAs will be achieved by incorporating components that are known to have sporicidal activity such as peroxy-generating powders (e.g., sodium percarbonate and sodium perborate) and/or neutral pH calcium hypochlorite. Both peroxy-generating powders and pH-adjusted hypochlorites are relatively non-corrosive. Once applied to a surface, the rheological and hygroscopic properties of the hydrogel component is expected to provide the desired chemical environment (thickness and moisture content) for an extended period of time, enhancing the efficacy of these active ingredients in killing the targeted microorganisms, fungi, bacteria, viruses, and spores.

Initiation of Task-5 has been delayed. The facilities required for the testing of BWA surrogate neutralization are in development. Receipt and installation of the biological testing equipment and reagents has started. Testing of various sporicidal components against the BWA surrogate *Bacillus subtilis* will commence upon completion of the delivery of the equipment/consumables required to perform the sporicidal efficacy evaluations.

## **7.1 Task 5(a) – Develop and Evaluate Formulations Comprising Components with Proven Biocidal and Sporocidal Activity**

Initial proof-of-concept evaluations of components with known sporocidal activity have started. These evaluations include incorporation of the percarbonate and perborate powdered compositions into the non-aqueous CWA neutralization solution (lanthanide catalyst systems) and evaluation of compatibility and stability of the two technologies. These tests have shown percarbonates and perborates to be stable in the current CWA neutralization systems (Component A). Addition of water, or the hydrogel template, dissolves and presumably activates the peroxy-generating species, producing hydrogen peroxide and/or peracetic acid in the presence of tetraacetylenediamine, in situ. The activation of stabilized peroxides is also being examined to determine the amount of activator required and the amount of peroxide generated in solution.

Lanthanide solutions that contain peroxy-generating components have been screened to evaluate if the CWA neutralization capability of the lanthanide catalyst system is negatively affected when these peroxy generating compounds are present. Notably, as these tests indicate, the lanthanide catalyst component (System 10) remains active against CWA simulants; in the presence of a peroxy-generating compound (sodium perborate), it demonstrated >99% decontamination efficacy against LG61 in solution. Additional details are given in Appendix 2.

An alternative method under this Task included the evaluation of lanthanum hypochlorite against LG61 to determine if the lanthanide ion retains its catalytic activity against CWAs when the counter anion is hypochlorite (as compared to the triflate ion in the traditional lanthanide catalysts systems). It was assumed that the hypochlorite ion would augment the neutralization activity against CWAs and at the same time, would act as a potent sporicide. Evaluations of the decontamination efficacy of such systems demonstrated poor results against LG61.

## **7.2 Task 5(b) – Test Formulations on BWA Bacteria and Spore Surrogate *Bacillus subtilis***

Evaluations of the sporicidal activity of formulations developed during this project have not yet started. BWA decontamination evaluation tests will start in the upcoming 5<sup>th</sup> Quarter.

## **7.3 Task 5(c) – Determine Required Physical and Chemical Properties of the Formulation Resulting in a 1-year Shelf-Life and 6-Log kill of *Bacillus subtilis* Surrogate Bacteria and Spores**

Task 5(c) has not yet started.

## **8. Tasks 6 & 7 (0% Completed)**

**Task 6: Develop Formulations Combining the Technologies Developed in Tasks 4 and 5.**

**Task 7: Submit One or More Formulations to a Government Laboratory for Live Agent Testing Targeting a 6-Log Kill of *Bacillus anthracis* Bacteria and Spores**

Tasks 6 and 7 are not scheduled to begin until November of this year. However, an important relationship with researchers at the Edgewood Chemical and Biological Center (ECBC) has been formed. In preparation for the live agent testing and the incorporation of neutralization capability for biological warfare agents (BWAs) (2nd year effort), CBIP has been in communication with the Edgewood Chemical and Biological Center (ECBC) and CUBRC (Buffalo, NY). Dr. Garry Edgington (Chief Scientist, CBIP) and Larry Stack (President of Government and Defense, CBIP) visited ECBC to discuss the objectives of the current TATRC contract and additional collaborations. ECBC and CBIP executed a Cooperative Research and Development Agreement (CRADA) and a non-disclosure agreement (NDA). ECBC stated that the objectives of the current TATRC contract requirements are synergistic with ECBC's mission requirements and

that they are interested in jointly developing hydrogel-based BWA neutralization technologies with CBIP using current DeconGel product as a baseline. They note that the current TATRC contract will not be able to achieve the full investigation required for BWA kill technology simply because the full regimen of BWA live agent testing and evaluation has not been accounted for within the TATRC contract. Notably, ECBC holds BWA neutralization active ingredient knowledge and technology that they believe to be compatible with our hydrogel technology (DeconGel). ECBC and the Department of Homeland Security (DHS) have reviewed the current TATRC objectives regarding both CWA neutralization and BWA kill.

## **9. Future Work**

Future work for the 2<sup>nd</sup> year of this contract includes the incorporation of components with sporicidal activity into the CWA decontamination systems developed during this first year, with the ultimate objective being the development of a CBRN decontamination product that incorporates components able to neutralize Biological Warfare Agents (BWAs) while retaining the effectiveness of the CWA neutralization catalysts and the radiological/TIC decontamination properties of DeconGel. The incorporation of various peroxide and peracetic acid generating technologies into both Component A and Component B of the formulations developed has been undertaken on an observational level monitoring the combinations for stability, undesired side reactions, and their ability to provide targeted concentrations of peroxide or peracetic acid. Future work includes: analytical/chemical method development for the determination of peroxide/peracetic acid concentrations in basic solution,; testing of CWA neutralization solutions in vials and on substrates to determine if their CWA neutralization efficacy in the presence of sporicidal/biocidal components has been affected; and the determination of sporicidal/biocidal activity of said solutions via evaluations against BWA surrogates (*B. Subtilis* spores).

Screening of co-solvents, surfactants, and other additives in an effort to improve the decontamination efficacy of the decontamination systems developed to date and the continued evaluation of one and two component systems on a variety of substrates will continue during the 2<sup>nd</sup> year. Upon completion of first round live agent testing, assessment of the results will provide

information pertinent to the optimization of formulations effective in the decontamination of live chemical warfare agents. Initial proof-of-concept tests on the stability of formulations comprising both CWA and BWA neutralizers has started and will continue during future efforts. Upon the development of a solution or system with adequate CWA and BWA neutralization/decontamination efficacy, long-term stability studies will commence.

## **10. Key Research Accomplishments**

- Developed CWA neutralization (one-component) systems demonstrating 99%+ destruction of CWA simulants in solution tests.
- Developed CWA neutralization (one-component) systems achieving or approaching a 2-log reduction (99% decontamination) of initial challenge on a variety of substrates.
- Developed a catalyst system that demonstrates fast neutralization rates in the presence of water (99%+ destruction of VX simulant in the presence of 50% water by volume).
- Developed and demonstrated compatibility between the CWA neutralization catalyst system and the hydrogel (DeconGel) component.
- Developed two-component decontamination systems that can physically remove radioactive isotopes, TICs and other contaminants from substrates achieve or approach a 2-log reduction (99% decontamination) of initial CWA challenge on a variety of substrates.
- Demonstrated significant decontamination efficacy against the VX simulant on sorptive substrates such as SBR and CARC, approaching 99% decontamination.
- Conducted initial proof of concept studies demonstrate compatibility between BWA neutralizers (known sporicidal components) and the CWA neutralization systems developed to date.

## **11. Reportable Outcomes**

CBIP and ECBC have co-authored and submitted a proposal to DHS for the further development and testing of formulations with BWA kill capability and CBRN decontamination efficacy.

## 12. Conclusions

The development of several formulations (both one-component and two-component systems) that demonstrate significant neutralization efficacy against VX, G-agents, and mustard gas simulants in solution and in substrate testing has been achieved. Screening evaluations of a variety of catalyst systems against CWA simulants performed during the initial quarters (Quarters 1 and 2) of this initiative demonstrated that the lanthanide catalyst systems had superior performance as compared to the other catalysts under evaluation. These lanthanide catalyst systems were further modified via adjustment of the type/concentration of lanthanide ion salts and/or the incorporation of a variety of components such as co-solvents, emulsifiers, and other additives to improve their neutralization efficacy on a variety of contaminant/substrate combinations. These modifications have resulted in the development of lanthanide catalyst systems that show enhanced neutralization rates against CWA simulants when used as one-component systems (independent of the hydrogel component) or as two-component systems when combined with the DeconGel hydrogel template (either mixed before use or applied in sequence).

Decontamination efficacies of improved lanthanide catalyst systems (one-component system, Component A) in solution tests and on a variety of substrates against CWA simulants are summarized in Table 7. This table demonstrates that a 2-log reduction of initial challenge, when these lanthanide catalyst systems are used independently of the hydrogel component, has been achieved (or approached) for most CWA simulant/substrate combinations tested. VX (and its simulants) is considered to be one of the most persistent and most difficult Chemical Warfare Agents (CWAs) to hydrolyze/neutralize (7, 8). Solution test evaluations against the G-agent simulant (DPPC) as well as the mustard agent simulant (CEES) demonstrate that they are readily neutralized by lanthanide ion catalyst systems or components thereof. Substrate testing of the lanthanide systems against G-agents and mustard gas simulants will commence in the upcoming quarter; it is anticipated that these CWA simulants will be readily neutralized, achieving >99% on these substrates.



**Table 7 - Decontamination Efficacies of Lanthanide Catalyst Systems (Component A) in Vial and Substrate Tests against CWA Simulants**

Test Environment	VX Simulant	G-Agent Simulant	Mustard Gas Simulant
	LG61 Decontamination Results	DPPC Decontamination Results	CEES Decontamination Results
<b>Vial/Solution</b>	>99.9% (1)	>95% (5)	99.1% (6)
<b>CARC*</b>	81.0% (2) - 99.4% (3)	TBD	TBD
<b>Rubber (SBR)</b>	91.4% (4)	TBD	TBD
<b>Stainless Steel</b>	95.5(4)	TBD	TBD

- (1) System 10.2, 10 minute contact time  
(2) System 10.2, 2 hour contact time  
(3) System 8 (100mM), 10 min contact time  
(4) System 10.2, 2 hour contact time  
(5) System 4, <5 minute contact time, analyte not detected  
(6) Ethanolamine only (main solvent in the lanthanide catalyst system), 24 hour contact time

An inherent disadvantage of lanthanide based catalyst systems is the reduction of their catalytic (for phosphonate transesterifications) efficacy in the presence of water. A notable achievement of this work includes the development of an improved lanthanide catalyst system (Component A) that demonstrates fast neutralization rates and tolerance to water (>99% destruction of LG61 in the presence of 50% water by volume). This system is a mixture of two salts (lanthanum and samarium triflates) and combines the fast neutralization rates of the lanthanum system and the tolerance to water of the samarium system. This achievement expands the versatility of these catalyst systems as it further broadens the conditions under which the catalyst is effective (e.g., damp/wet). It also offers the option to utilize them in combination with the water-based hydrogel component (Component B) both in premixed systems (the two components are mixed at the spray tip) or systems that are applied sequentially (application of Component A followed by the application of Component B).

LG61 has been the main CWA simulant of interest during formulation development since VX and its simulants are the most difficult to neutralize/decontaminate (7, 8). The table below

summarizes decontamination efficacies of two-component systems comprising lanthanide catalyst systems (Component A) mixed or applied in sequence with the hydrogel component (DeconGel 1128, an improved sprayable version of CBIP's decontamination product) against LG61 on a variety of substrates.

**Table 8 - Decontamination Efficacies of Two-Component Systems (Component A & Component B) mixed before use or applied sequentially on a variety of substrates against LG61 (VX simulant)**

Substrate	Two-Component Decontamination Systems mixed before use	Two-Component Decontamination Systems applied sequentially
	VX Simulant (LG61) Decontamination Results	VX Simulant (LG61) Decontamination Results
<b>CARC</b>	95.6% (1) - 99.6% (2)	95.6% (5) - 99.8% (6)
<b>Rubber (SBR)</b>	96.4% (3)	TBD
<b>Stainless Steel</b>	99.9% (4)	99.9% (5)

(1) System 10.2 mixed with DeconGel 1128 before use

(2) Modified System 8 (100mM, 20/80 THF/Ethanolamine) mixed with DeconGel 1128 before use

(3) System 10.2 mixed with DeconGel 1128 before use

(4) System 10.2 mixed with DeconGel 1128 before use

(5) Sequential application of System 10.2 followed by DeconGel 1128

(6) Sequential application of Modified System 8 (100mM, 20/80 THF/Ethanolamine) followed by DeconGel 1128

The DeconGel hydrogel template has the ability to encapsulate and physically remove radioactive isotopes and Toxic Industrial Chemicals (TICs) from a variety of porous and non-porous substrates. A two component decontamination system that can decontaminate CWAs (Component A) and radioactive isotopes/TICs (Component B) provides the end user with several options: applying either component independent of the other when the threat is known; combining the two components in sequence or as a pre-mixed emulsion when the threat is unknown or when concurrent threats are present (e.g., radioactive isotopes and CWA threats from a 'dirty bomb').

The above two tables indicate impressive decontamination performance for the decontamination systems developed thus far, approaching or achieving the objective of the 2-log reduction of initial challenge on various substrates. An important achievement of the work to date has been the significant decontamination efficacy on Styrene Butadiene Rubber (SBR) substrates. Recently developed formulations demonstrate decontamination efficacy of >91% after 2 hours for a one-component system, and >96% after 24 hours for a two-component system mixed at the point of use against LG61 on SBR. SBR is a notoriously difficult to decontaminate substrate due to its porous, sorptive, and hydrophobic nature. These results are extremely promising; current evaluations aimed at identifying co-solvents, surfactants, and other additives that are able to penetrate into hydrophobic and sorptive substrates are expected to further enhance the decontamination efficacy on rubber (i.e., approaching a 2-log reduction of the initial challenge).

The majority of testing has been performed on panels coated with Chemical Agent Resistant Coating (CARC). CARC, though more resistant to CWAs relative to other types of paint, is a highly porous and sorptive material that is difficult to decontaminate. An unexpected result observed during evaluations on CARC coated coupons was the relatively large variation in the decontamination efficacy results of the lanthanide catalyst systems against LG61 on CARC coupons acquired/prepared from different sources. Efficacy results for one and two component decontamination systems have ranged from ~80% to 99%+ for evaluations performed on different batches of CARC coated coupons. To date, no satisfactory explanation has been determined for these decontamination efficacy inconsistencies on CARC coated coupons. Development efforts continue to focus on determining the reason for the reduced decontamination efficacy results on CARC, and separately, on evaluation of additional co-solvents and additives that are expected to enhance the decontamination efficacy on CARC and other sorptive substrates.

While two-component systems (mixed at the point of use, or applied sequentially) show decontamination efficacies of >99% against LG61 on stainless steel (SS), the lanthanide catalyst system (Component A) shows <99% efficacies on SS (2 hours of contact) when it is used independently of the hydrogel component. Recent tests performed on glass slides indicate that the reason for these lower efficacies on non-porous substrates may be originating from the

surface tension of the CWA simulant (LG61 remains in the form of a droplet when applied on glass and steel). The result is a local concentration of CWA far greater than the 50:1 decontaminant to contaminant challenge target. Techniques to better dissolve the CWA as well as to apply a thicker layer of neutralization solution on the substrate are currently being developed. These techniques are expected to improve neutralization efficacies against CWAs on non-porous substrates. Additional evaluations in determining the efficacy of one-component systems on non-porous substrates after longer contact times are currently underway; initial screening of a modified lanthanide catalyst system on SS demonstrates decontamination efficacies >99.9% after 24 hours of contact time.

The current initiative also includes the ultimate objective of developing a single CBRN decontamination product that incorporates components able to neutralize Biological Warfare Agents (BWAs) while retaining the effectiveness of the CWA neutralization catalysts and the radiological/TIC decontamination properties of DeconGel. Initial experiments incorporating sporicidal components (peroxy-generating species) into Component A (the non-aqueous CWA neutralization solution) demonstrate that these chemistries are compatible and stable (for at least 1 week). Addition of water or the hydrogel template (Component B) into Component A above dissolves and (presumably) activates the peroxy-generating species. Lanthanide solutions containing peroxy-generating components have been screened to determine if the CWA neutralization capability of the lanthanide catalyst system is negatively affected when these peroxy-generating compounds are present; initial tests indicate the lanthanide catalyst component remains active (>99% decontamination efficacy against LG61 in solution tests) in the presence of a peroxy-generating compound (sodium perborate). Future work includes incorporating components with known sporicidal activity into the CWA decontamination systems developed to date (both one- and two-component systems), and evaluating their decontamination efficacy against CWAs and their sporicidal efficacy against BWA surrogates (*Bacillus subtilis* spores).

CBIP and CUBRC (the lab performing the live CWA testing) are currently finalizing details for the first set of live agent testing. CWA simulants used in this study are less reactive than their live agent counterparts. Formulations that provide neutralization/decontamination results that

achieve or approach the decontamination objective (2-log reduction of initial challenge) are anticipated to demonstrate equal or better results when tested against live agents.

No change in the scope of the project is recommended or requested.

### 13. References

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## **14. Appendices**

Appendix 1: Method Development and General Sampling Procedure

Appendix 2: Supplemental Testing Results

**Appendix 1:**  
**Method Development and General Sampling Procedure**

## Method Development

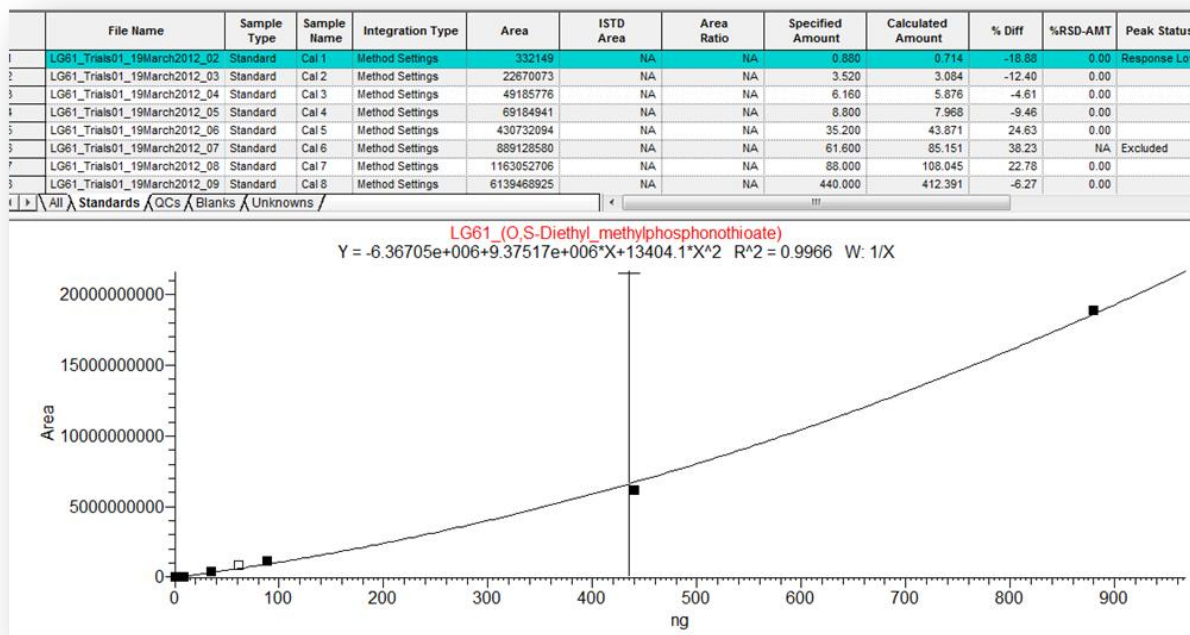
Due to the variability of the neutralization systems developed in this project, extensive method development has been executed during this reporting period. A typical procedure for the preparation of the CWA simulant analytical standards is the following:

- 1) An aliquot of a known volume of the simulant of interest is added to a tared volumetric flask and weighed, the sample is then diluted volumetrically to produce a stock solution from which a calibration curve and/or other QC standards are prepared.
- 2) Portions of the stock solution and subsequent dilutions are dispensed and diluted to final volumes such that a minimum of nine calibration samples are prepared.
- 3) Standards of concentrations different from those in the calibration set may also be prepared in the same manner for use as QC reference standards.

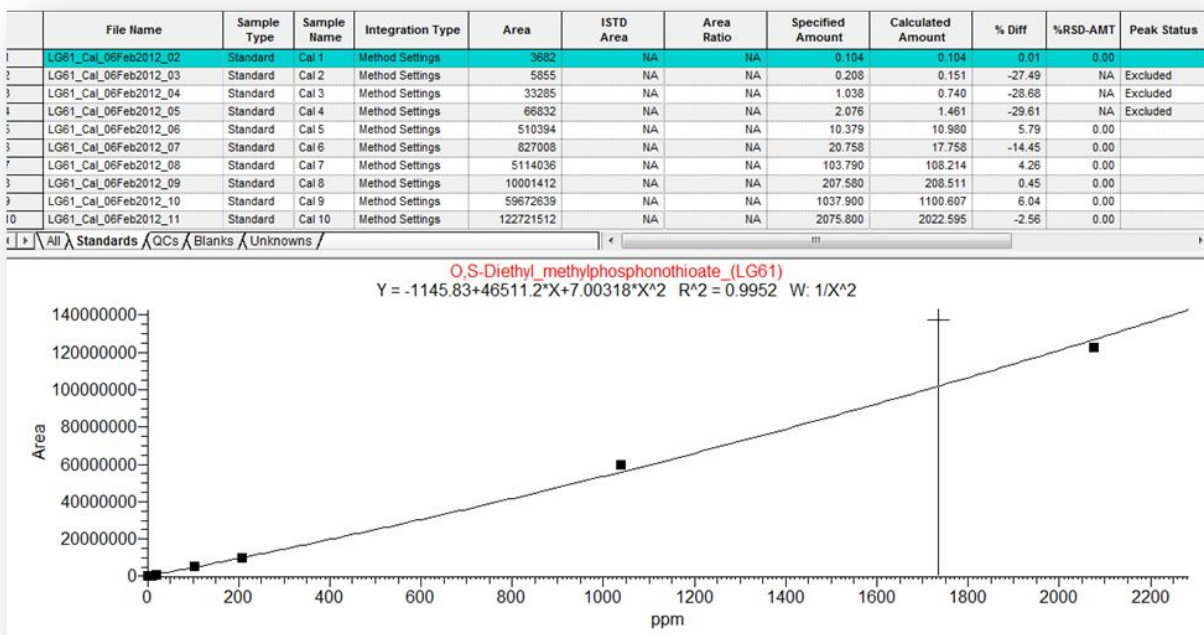
An LC/MS and a GC/MS are currently employed in the quantitative analysis of CWA simulants. A Thermo Trace GC Ultra/DSQ II MS with auto-sampler is used to analyze DPPC, CEES and LG61 for all neutralization system screening and decontamination samples. A Thermo Surveyor Plus (HPLC)/LCQ Deca XP Plus (MS) is also used to analyze LG61 concentrations for all neutralization system screening and decontamination samples. Representative calibration curves for LG61 analyzed by GC/MS and LC/MS can be seen below.



## Representative LC/MS Calibration Curve for LG61



## Representative GC/MS Calibration Curve for LG61



Replacement of the GC/MS analytical column was paramount to the improvement of the analytical methods being used to quantify the destruction of CEES and LG61. CEES method development to date has provided a limit of detection improvement from ~30ppm (parts per million) to 0.036ppm, an improvement of nearly three orders of magnitude while maintaining an upper limit of ~1500ppm, enabling the accurate determination of decontamination efficacies of up to 99.997%. Similarly, the improved GC/MS method for the analysis of LG61 provides a limit of detection of 0.034ppm and a corresponding upper limit of approximately 2000ppm enabling the accurate determination of decontamination efficacies of up to 99.998%. The representative calibration curve for LG61 by GC/MS above provides a graphical representation of a 10 point calibration curve analyzed for the quantitative determination of LG61, due to scaling not all data points are distinctly visible. An LC/MS method for the quantitative analysis of LG61 has also been developed with quantification limits ranging from about 0.7ppm up to ~1000ppm with an analysis time of only 5 minutes per sample. The representative calibration curve for LG61 by LC/MS above provides a graphical representation of an 8 point calibration curve analyze, due to scaling not all calibration data points are distinctly visible.

## **Sample Preparation**

Screening of neutralization systems against DPPC, LG61 and CEES was conducted as described below. All screening trials were conducted at a volume ratio of decontaminant to contaminant of 50 to 1 which is the military standard of decontaminant to contaminant ratio utilized for the evaluation of decontamination technologies against CWA. All vial testing samples are prepared with a known amount of CWA simulant, 2uL is typically used unless otherwise required by the testing. All substrate trials were also conducted at a decontaminant to contaminant volume ratio of 50 to 1. All substrate testing samples are prepared with a known amount of CWA simulant, 10uL or 20uL is typically used, dependant on substrate surface area, unless otherwise required by the testing. As a result of the variability of the neutralization systems evaluated in this project, only the general method for standard and sample preparation will be discussed below.

### **General Preparation for Vial Testing:**

Equipment Utilized:

- Volumetric flask
- 10μL syringe
- 1.8mL auto-sampler vials
- Sample vials
- 250μL syringe
- 500μL syringe
- 100-1000μL Auto-pipette w/disposable tips
- 20-200μL Auto-pipette w/disposable tips
- Solvent(s) - HPLC grade or better
- Chemical neutralization system(s) of interest

- 1) An aliquot of a known volume of a CWA simulant is added to a tared sample vial and the weight of the stimulant was determined.
- 2) The respective neutralization system is then added to the sample vial at a decontaminant to contaminant volume ratio of 50 to 1 and allowed to remain in contact for a prescribed amount of time.

- 3) The reaction mixture is then quenched with an appropriate quenching agent (refer to later sections of this report for quenching methods), transferred to an auto-sampler vial and analyzed by GC/MS or LC/MS.

### **General Preparation for Substrate Testing:**

Equipment Utilized:

- 10 $\mu$ L glass syringe
- Disposable 1mL polypropylene syringes
- Extraction solvents, HPLC grade or better
- 16oz Qorpak jars

Experimental decontamination sampling and controls (positive and negative) were conducted on CARC, stainless steel and rubber coupons in triplicate.

### **General Sample Procedure**

Upon addition of 10 or 20 $\mu$ L of CWA simulant (experimental samples and positive controls) to coupon surfaces, contaminated coupons were placed under an inverted 16oz, wide mouth Qorpak jar for 60 min, and then either a) placed in extraction solvent via extraction reservoir (for positive controls), or b) a prescribed volume of decontaminant was applied evenly over the coupon surface area and the coupons were allowed to stand for the allotted contact time. At the end of the contact time the reaction was quenched by placing the decontaminated coupon in an extraction container pre-filled with 20mL of extraction solvent (plus an aliquot of acetic acid as a quenching agent as required by the sample) so that the coupon is completely immersed in the extraction solvent. The extraction bottle was then capped and swirled to facilitate contaminant extraction and let stand for 60 minutes. Extraction solvent was then directly placed in an auto-sampler vial for direct analysis with no further sample preparation or manipulation.

### **Negative Control Procedure**

For negative controls, no contaminant was applied to coupon surfaces. Instead the appropriate volume of a chemical neutralization system was dispensed on the coupon surface and the general procedure as described above was followed.

### **Positive Control Procedure**

For positive controls, 10 or 20 $\mu$ L of LG61 was applied to coupon surfaces then covered with an inverted glass Qorpak jar for 60min of coupon-contaminant “incubation” time. After the appropriate incubation time, no decontaminant was applied and contaminated coupons were immediately placed in an extraction reservoir pre-filled with 20mL of extraction solvent. The extraction bottle was then capped and swirled to facilitate contaminant extraction and let stand for 60 min. Extraction solvent was then directly placed in an auto-sampler vial for direct analysis with no further sample preparation or manipulation.

### **Dose Control Procedure**

Dose control samples are used to measure the mass dispensed of the selected simulant by the dispensing tool. They are also used to calculate the extraction efficiency of an analyte/solvent/substrate system. Dose control samples are prepared by drawing 10 or 20 $\mu$ L of simulant into the dispensing tool, dispensing the analyte directly into the prescribed amount of extraction solvent and measuring the concentration by GC/MS or LC/MS. Extraction efficiency is calculated by calculating the percent difference between dose control and positive control samples.

### **Chromatographic Analysis**

The GC/MS and LC/MS methods described above were used to determine residual concentrations of CWA simulants in solutions and on decontaminated substrates.

## **Appendix 2:**

### **Supplemental Testing Results**

## Preliminary Co-Solvent Testing

### Solvent–Rubber Interaction Observations

Solvent Screened	Mass of Rubber Coupon	Mass of Rubber (After 1-hour Immersion)	% Weight Increase	Mass of Rubber (After 24-hour Immersion)	% Weight Increase
Ethanolamine	1.6837	1.6877	0.24	1.6915	0.46
Ethylene glycol monobutyl ether	1.8185	1.8526	1.88	1.9569	7.61
Hexanes	1.8480	2.0820	12.66	2.1619	16.99
Dipropylene glycol methyl ether	1.8406	1.8697	1.58	1.9563	6.29
NMP	1.8133	2.1615	19.20	3.2714	80.41
Trichloroethylene (Perc)	1.7952	5.2510	192.50	6.9024	284.49
THF	1.9145	4.0500	111.54	5.0438	163.45
Ethyl lactate	1.7000	1.7257	1.51	1.8003	5.90
Gentech (n-Propyl bromide)	1.7389	4.2127	142.26	5.7864	232.76
Novec 7100 (Methoxy nonafluorobutane)	1.7725	1.7706	-0.11	1.7638	-0.49
Ensolv (n-Propyl bromide)	1.8926	4.5698	141.46	6.0020	217.13
Leksol (n-Propyl bromide)	1.8458	4.5583	146.96	6.2732	239.86
DMSO	1.9145	1.9322	0.92	1.9906	3.97
ACN	1.7461	1.7763	1.73	1.8654	6.83
Limonene	1.7612	2.2118	25.58	3.2959	87.14

NMP – 1-Methyl-2-pyrrolidone

THF – Tetrahydrofuran

DMSO – Dimethyl sulfoxide

ACN - Acetonitrile

### Lanthanum Triflate-Solvent Miscibility Observations

Solvent Screened	2-Hour Observation	16-Hour Observation	24-Hour Observation
<b>Ethanolamine</b>	gummy, a little cloudy	similar, still cloudy	gummy mostly dissolved
<b>Ethylene glycol monobutyl ether</b>	dissolved	dissolved	dissolved
<b>Hexanes</b>	Not dissolved	slightly more dissolved	still cloudy with particles
<b>Dipropylene glycol methyl ether</b>	dissolved	dissolved	dissolved
<b>NMP</b>	some particles still	dissolved	dissolved
<b>Trichloroethylene (Perc)</b>	Not dissolved	still cloudy not dissolved	not dissolved
<b>THF</b>	dissolved	dissolved	dissolved
<b>Ethyl lactate</b>	dissolved	dissolved	dissolved
<b>Gentech (n-Propyl bromide)</b>	not dissolved	dissolved	dissolved
<b>Novec 7100 (Methoxy nonafluorobutane)</b>	not dissolved, cloudy	not dissolved, cloudy	not dissolved
<b>Ensolv (n-Propyl bromide)</b>	just slightly dissolved	slightly more dissolved	approx. 30% dissolved
<b>Leksol (n-Propyl bromide)</b>	Not dissolved	mostly dissolved, 1 or 2 particles remain	dissolved
<b>DMSO</b>	Dissolved	dissolved	dissolved
<b>ACN</b>	just a few particles remain	dissolved	dissolved
<b>Limonene</b>	cloudy slightly dissolved	still cloudy slightly dissolved	still cloudy slightly dissolved

See preceding table notations for chemical abbreviations.



### DeconGel-Solvent Miscibility Observations

Solvent Screened	Miscibility with DeconGel 1128
Hexanes	Immiscible
NMP	Miscible
Trichloroethylene (Perc)	Immiscible, forms slight emulsion
THF	Miscible
Leksol (n-Propyl bromide)	Immiscible, forms slight emulsion
Limonene	Immiscible, forms slight emulsion

See preceding table notations for chemical abbreviations

**Neutralization Efficacy of Perborate Containing Lanthanide Catalyst Solutions Against LG61 in Solution**

Neutralization System Tested	Contact Time	Calculated Concentration (ppm)	Analytical Result (ppm)	% Neutralization	Average % Neutralization	% Std. Dev.
System 10	1h	998.920	0.487	99.95	99.95	0.00*
			0.529	99.95		
			0.496	99.95		
System 10 + 60mM Sodium perborate (NaBO <sub>3</sub> ) - 'Activated'	1h	1187.905	8.888	99.25	99.27	0.02
			8.626	99.27		
			8.362	99.30		
System 10 + 60mM NaBO <sub>3</sub> - 'Un-activated'	1h	1295.896	6.324	99.51	99.50	0.02
			6.735	99.48		
			6.349	99.51		
System 10-TD (prepared in 8:1:1 ETA/THF/DMOM)	1h	1130.389	0.706	99.94	99.94	0.00
			0.665	99.94		
			0.687	99.94		
System 10-TD + 60mM NaBO <sub>3</sub> - 'Activated'	1h	959.147	33.166	96.54	96.58	0.03
			32.725	96.59		
			32.597	96.60		
System 10-TD + 60mM NaBO <sub>3</sub> - 'Un-activated'	1h	981.350	n/d	99.98	99.98	0.00*
			n/d	99.98		
			n/d	99.98		